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Veenvliet, Hendrik; Wiersma, Douwe A.

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STARK EFFECTS ON THE B_{1g} AND A_u $n\pi^*$ TRIPLET STATES OF *p*-BENZOQUINONE

Hendrik VEENVLIET and Douwe A. WIERSMA
Laboratory for Physical Chemistry, University of Groningen, Groningen, The Netherlands

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The results of polarized Stark effect absorption experiments on the lower triplet states of *p*-benzoquinone (PBQ)-h_4 and -d_4 in single crystals at 1.8°K are reported. These measurements give strong support for the assignment of the lowest triplet state as triplet $^3B_{1g}$ ($n\pi^*$). The origin of this state in PBQ-h_4 is observed as an electric field induced transition at 18602.8 cm^{-1} and is interpreted as the g-inversion level of a double-minimum potential well. The line observed at 18619.7 cm^{-1} in the PBQ-h_4 crystal is therefore assigned as the u-inversion level of this double well with A_u ($B_{1g} \otimes b_{1u}$) total symmetry. Its intensity manifests the strong vibronic coupling that occurs among the B_{1g} and A_u $n\pi^*$ triplet states along b_{1u}-type nuclear motions.

1. Introduction

One of the most puzzling features of the *p*-benzoquinone-h_4 [PBQ; $L = z(B_{1u}), M = y(B_{2u})$] low-temperature pure crystal absorption spectrum is the appearance of a weak triplet absorption at 18619.7 cm^{-1}. This line, only separated by 327 cm^{-1} from a much stronger absorption at 18947 cm^{-1} in the pure crystal, whose interpretation as the ^3A_u ($n\pi^*$) origin seems unquestionable, has been the subject of some very detailed spectroscopic work in both pure and mixed crystals over the past decade. From a detailed analysis of the PBQ absorption spectrum in different hosts Klump [1] and McClure [2] concluded this absorption to be the crystal field induced origin of the lowest benzene like $^3B_{1u}$ ($\pi\pi^*$) triplet state. Such an assignment is indeed in agreement with the results of recently performed ab initio SCF calculations [3] on PBQ. Koyanagi et al. [4], however, concluded from a vibrational analysis of the phosphorescence spectrum of PBQ in an isotopically mixed crystal, that the lowest triplet state in the crystal at 18619.7 cm^{-1} was the origin of the $^3B_{1g}$ ($n\pi^*$) triplet state. Trommsdorff [5], from a detailed study on PBQ and some methylsubstituted *p*-benzoquinones also concluded the lowest observed triplet state to be the $^3B_{1g}$ ($n\pi^*$) state. Such an assignment, however, does not explain the appearance of this state as an origin, as inversion symmetry in the pure crystal is preserved at the molecular site. We therefore have performed a thorough absorption and Stark effect study on both pure and isotopically mixed crystals of PBQ to obtain more information on the nature of the lower electronic states of PBQ.

In a previous paper [6]† we have shown that the lowest B_{1g} ($n\pi^*$) singlet state absorption spectrum of PBQ can be consistently interpreted assuming this state to have acquired a double-minimum potential along one (or more) b_{1u} normal modes. In this paper we will show that Stark effect measurements on the triplet states give strong support for the assignment of the lowest triplet state as triplet $^3B_{1g}$ ($n\pi^*$). The line observed at 18619.7 cm^{-1} in PBQ-h_4 however is *not* the origin of the spectrum, but a vibronic level of ^3A_u ($^3B_{1g} \otimes b_{1u}$) total symmetry. The origin of the $^3B_{1g}$ ($n\pi^*$) system in PBQ-h_4 is found as an electric field induced transition at 18602.8 cm^{-1} and is interpreted as the forbidden (spin and space) *g*-inversion level of a double-minimum potential.

† Johnson and Trommsdorff [7] have independently reached a similar conclusion.

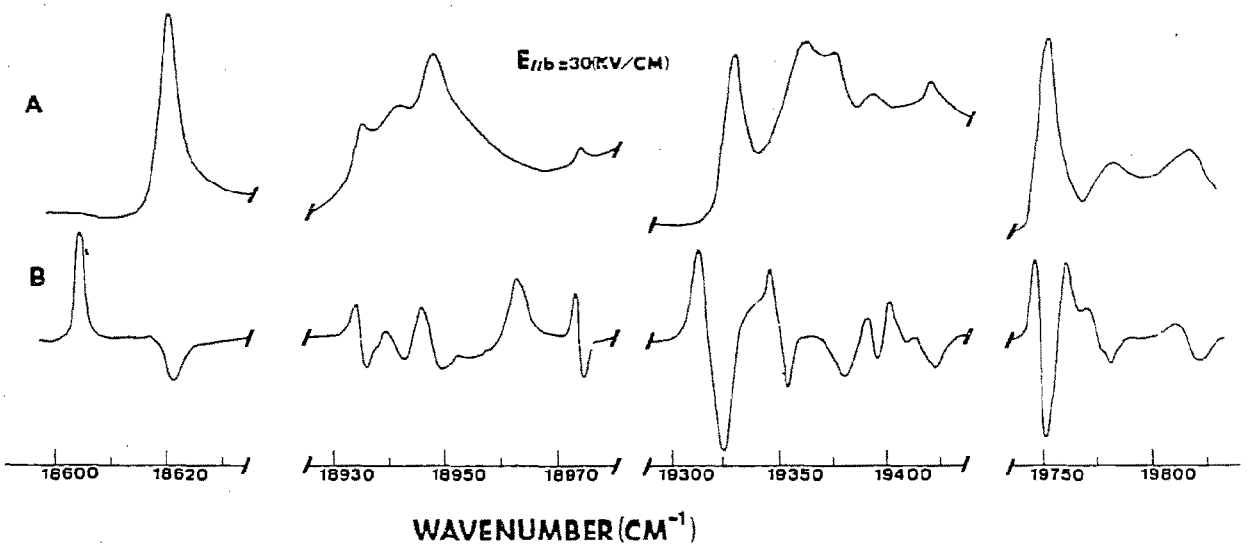

Fig. 1. Absorption (A) and electric field induced (B) spectrum of PBQ-h_4 in the lower triplet state regions. The electric field was 30 kV/cm and parallel to the crystal b axis. For the peak at 18619.7 cm^{-1} the light was polarized parallel to the crystal a axis. For the rest of the spectrum the light was polarized at 50° with respect to a axis in the ac'-crystallographic plane.

2. Results and discussion

With the $^3B_{1g}$ ($n\pi^*$) and ^3A_u ($n\pi^*$) states only separated by $\approx$320 cm^{-1} one expects these states to perturb one another very strongly so that under some conditions the lower state may acquire a double-minimum potential along one (or more) of the vibronically perturbing b_{1u}-modes. In a previous paper [6] we showed that this is exactly what happens for the lowest $^1B_{1g}$ ($n\pi^*$) state of PBQ. We will now show that this model also very elegantly explains the lowest triplet state absorption spectrum of PBQ and that indeed the lowest triplet state in PBQ is also of B_{1g} ($n\pi^*$) symmetry.

Fig. 1 shows the polarized Stark-modulated spectrum and the corresponding absorption spectrum of PBQ-h_4 at 1.8°K for an electric field parallel to the crystal b axis. Analogous results were obtained for PBQ-d_4 single crystals. The crystal structure of PBQ is such [8] that the crystal b axis is nearly in the molecular plane making an angle of 38° with the long molecular axis. We have also studied the Stark effect for electric fields parallel to the p(201)-axis of the crystal (the p-axis is also almost in the molecular plane and $p \wedge L = 52°$) and found similar though smaller Stark effects. No effects were observed for electric fields perpendicular to the cleavage (almost molecular) plane so that the Stark effect measured is definitely connected with a long axis (z) molecular transition moment.

As fig. 1 shows, in an electric field, the lowest observed triplet state absorption, e.g., in PBQ-h_4 at 18619.7 cm^{-1}, decreases in intensity and shifts to higher energy, while a line 16.9 cm^{-1} to the red of it is induced in an electric field. As polarized Zeeman experiments have shown the triplet absorption at 18619.7 cm^{-1} to be of ^3A_u ($n\pi^*$) total symmetry, the induced line is probed as a triplet state of B_{1g} total symmetry. We assign therefore this induced line as the *origin* and *g-inversion level* of the $^3B_{1g}$ ($n\pi^*$) triplet state. The inversion splitting in the origin thus amounts to 16.9 cm^{-1} for PBQ-h_4 and 13.4 cm^{-1} for PBQ-d_4. The g-inversion level remains strictly forbidden in the C_i-crystal field, but the u-inversion level is induced as a false origin onto the B_{1g} ($n\pi^*$) triplet state. Its intensity is another manifestation of the fact that the $^3B_{1g}$ ($n\pi^*$) and ^3A_u ($n\pi^*$) triplet states, in the presence of nuclear motions of b_{1u} symmetry, become strongly mixed.

Fig. 1 further shows that in the origin region of the second triplet state also intense electric field induced lines are found at 18963.5 cm^{-1} (PBQ-h_4) and

18982.0 cm^{-1} (PBQ-d_4). We correlate these lines with u-inversion levels of u-vibrations built onto the $^3B_{1g}$ ($n\pi^*$) state. The observed inversion splittings of 23 cm^{-1} (PBQ-h_4) and 18 cm^{-1} (PBQ-d_4) for these levels are significantly larger than the origin inversion splittings. This is of course what is expected, all u-type modes being mixed in the C_i-crystal field, so that on excitation of any mode the barrier height for tunnelling into the equivalent conformations should decrease. There are some levels, built onto the lowest $^3B_{1g}$ ($n\pi^*$) state that only show minor intensity changes, but significant shifts in an electric field. In these vibronic states, the inversion splittings must be quite large. These effects show that for the $^3B_{1g}$($n\pi^*$) state the barrier height for inversion must be considerably lower than for the corresponding B_{1g} ($n\pi^*$) singlet state.

Comparing now the PBQ-h_4 and -d_4 spectra in the region of the second triplet state we find that the lines just below the electronic origin of the second [^3A_u ($n\pi^*$)] triplet state show a considerable drop in intensity on deuteration. We suggest therefore that these lines have acquired their intensity through interference with the strongly allowed ^3A_u ($n\pi^*$) state. This point certainly deserves further study and we plan to carefully study this effect on partly deuterated isotopes of PBQ.

Fig. 1 also shows that the origin of the second ^3A_u ($n\pi^*$) triplet state shifts to lower energy in an electric field. This is exactly what is expected. Although this level will be pushed upward through repulsion of the $^3B_{1g}$ ($n\pi^*$) origin, it will be pushed downward by all vibronic additions of the correct symmetry built onto this origin at higher energy. Finally we want to draw attention to the absorptions near 19365 cm^{-1} in PBQ-d_4. As can be seen from fig. 2, a weak line at 19380 cm^{-1} shows a drastic Stark effect, in that it is shifted to higher energy and a new line is induced at 2.3 cm^{-1} to lower energy. We suggest this effect to be due to an accidental degeneracy of a level built onto the lowest B_{1g} ($n\pi^*$) triplet state and a level built onto the second A_u ($n\pi^*$) triplet state. A similar effect is not found in the spectrum of PBQ-h_4.

3. Conclusion

There is now direct proof, from Stark effect measurements, that the lowest triplet state in PBQ is a $^3B_{1g}$ ($n\pi^*$) state. The strong vibronic coupling of this state with the nearby ^3A_u ($n\pi^*$) state manifests itself in the double-minimum potential that the lower state has acquired along b_{1u}-type nuclear motions and these motions also induce the origin u-inversion level observed in the absorption spectrum.

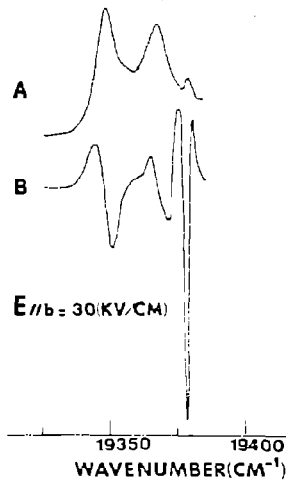

Fig. 2. Absorption (A) and Stark modulated spectrum (B) of PBQ-d_4 near 19365 cm^{-1}. The electric field was 30 kV/cm and parallel to the crystal *b* axis. The light was polarized parallel to the crystal *a* axis.

Several questions remain to be answered.

(i) Which b_{1u}-modes are predominantly active in the vibronic coupling process?

(ii) What are the barrier heights for inversion in both the triplet and singlet B_{1g} ($n\pi^*$) states?

(iii) Where is the B_{1u} ($\pi\pi^*$) triplet state located?

A detailed analysis of the phosphorescence spectrum of PBQ should aid in the identification of the "promoting" vibronic coupling mode. We are at present engaged in such a study and also plan to investigate the Stark effect on isotopically substituted *p*-benzoquinones as to further analyze the absorption spectra. A phosphorescence excitation spectrum of gaseous PBQ might locate the position of the benzene like $^3B_{1u}$ ($\pi\pi^*$)-state.

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